Van-der-Waals approximation of real gas

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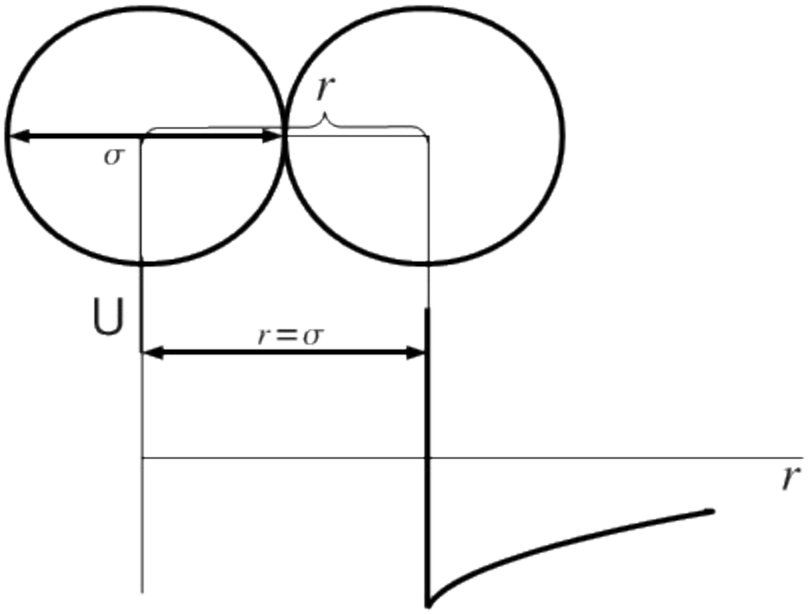
Hard spheres approximation

- Ideal gas:
  - No interactions
- Hard-speres
  - Excluded volume effect
  - Pairwise interactions

$$u(r) = \begin{cases} +\infty & r < \sigma \\ u_1(r) & r > \sigma \end{cases}$$



$$U(\mathbf{r_1}, \ldots, \mathbf{r_N}) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} u(|\mathbf{r_i} - \mathbf{r_j}|)$$

Excluded volume

Free energy of ideal gas

$$\mathcal{F}_{ideal} = Nk_BT \ln\left(N\Lambda^3/e\right) - Nk_BT \ln V$$

"Free of collisions" part of the volume:

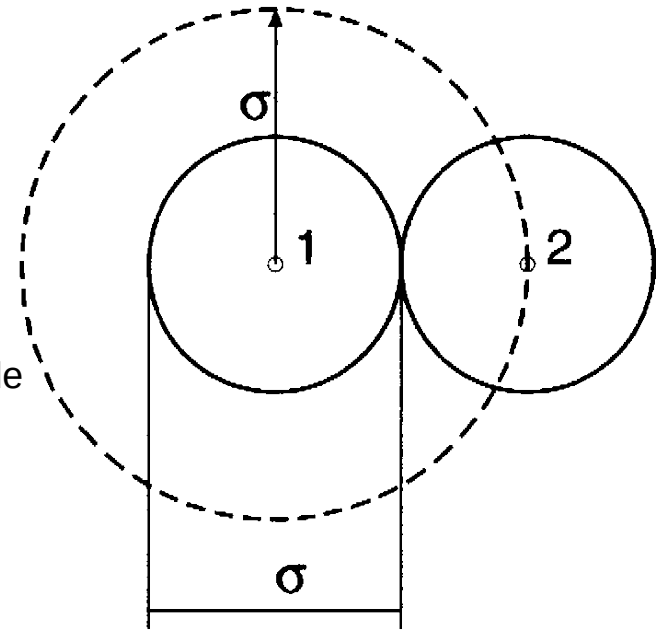
$$V_f = V - Nb$$

.b – excluded volume per particle

$$b = \frac{2}{3}\pi\sigma^3$$

(Per each two particles we exclude volume of sphere:)

$$\frac{4}{3}\pi\sigma^3$$



Free Energy of non-interacting spheres:

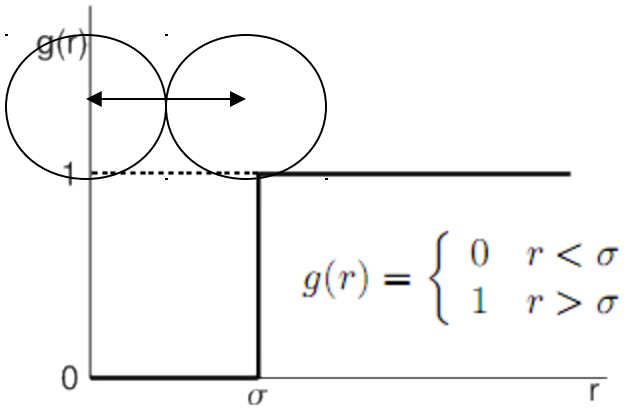
$$\mathcal{F}_0 = Nk_BT \ln\left(N\Lambda^3/e\right) - Nk_BT \ln(V - Nb)$$

Correction due to particles interaction

$$\mathcal{F} = \mathcal{F}_0 + \frac{1}{2} N \psi$$

Ψ - mean interaction energy of pair of particles

$$\psi = 4\pi n \int_0^\infty u(r) g(r) r^2 dr = -2 \frac{N}{V} a$$



RDF for hard spheres

$$a = -2\pi \int_\sigma^\infty u_1(r) r^2 dr$$

Van-der-Waals formula

$$\mathcal{F} = N k_B T \ln \Lambda^3/e - N k_B T \ln(V - Nb) - \frac{N^2}{V} a$$

$$P = -\frac{\partial \mathcal{F}}{\partial V} = -n^2 a + \frac{n k_B T}{1 - nb}$$

At the critical point:

$$\left.\frac{dP}{dV}\right|_{T_c} = \left.\frac{d^2 P}{dV^2}\right|_{T_c} = 0 \quad \Longrightarrow \quad b = \frac{1}{3n_c}, \quad a = \frac{9}{8}\frac{k_B T_c}{n_c}$$

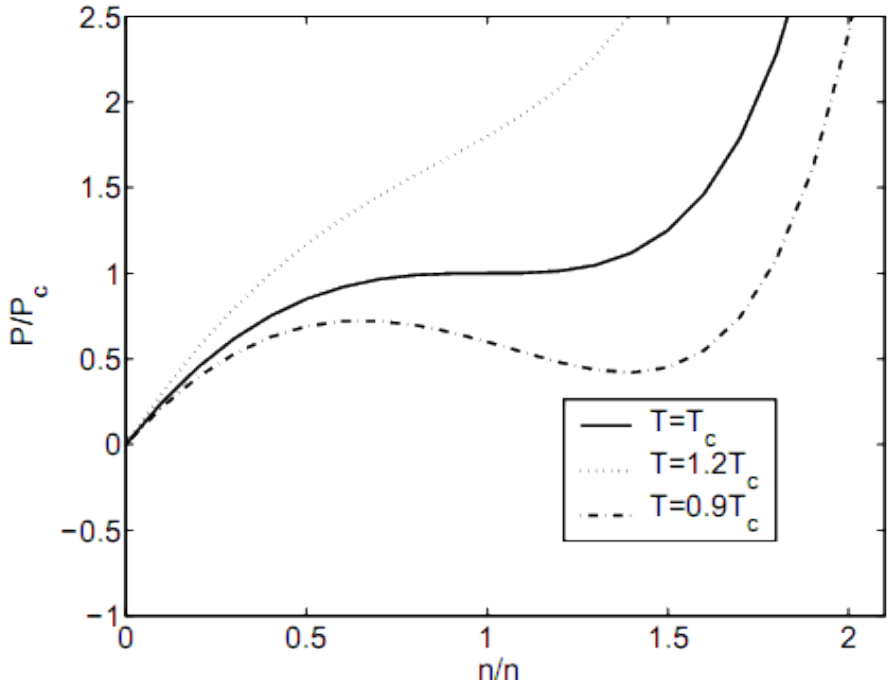
$$P^* = \frac{P}{P_c} \qquad n^* = \frac{n}{n_c} \qquad T^* = \frac{T}{T_c}$$

$$P^* = -3n^{*2} + \frac{8 n^* T^*}{3 - n^*} \qquad 0 < n^* < 3$$

Pressure

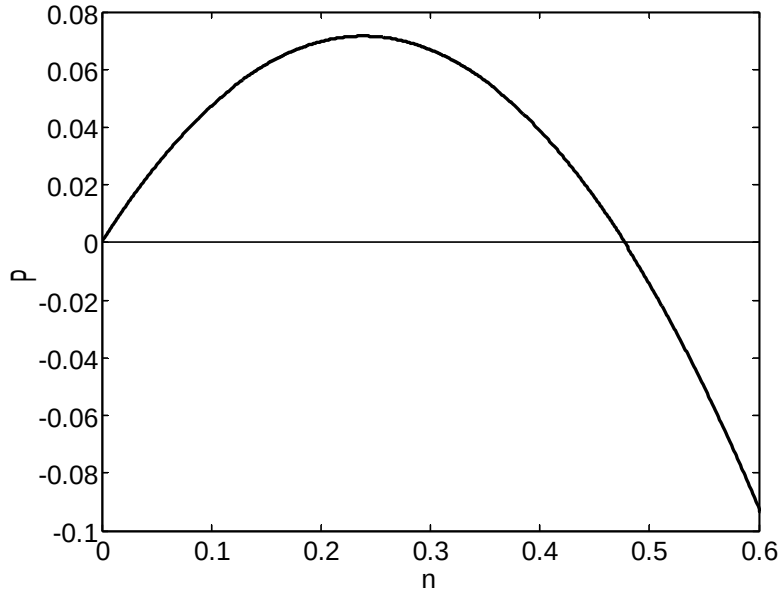
$$P^* = -3n^{*2} + \frac{8n^*T^*}{3 - n^*} \qquad 0 < n^* < 3$$

Van-der-Waals



Artificial RDF (1-βu)

$$P = nkT - \frac{8}{3}\pi n^2 \varepsilon \sigma^3 \left(\frac{2}{3} + \frac{16\varepsilon}{105kT} \right)$$



Units are inaccurate!!!!

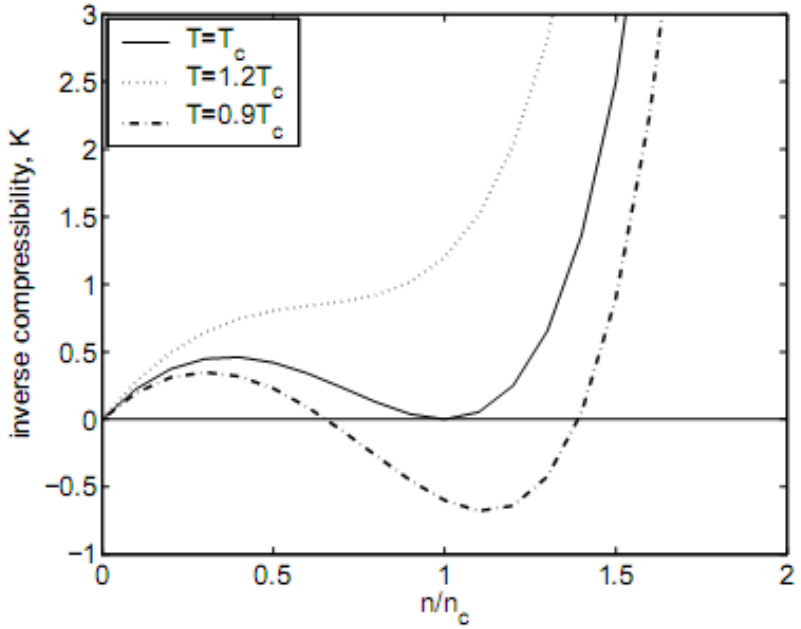
Inverse compressibility

Van der waals

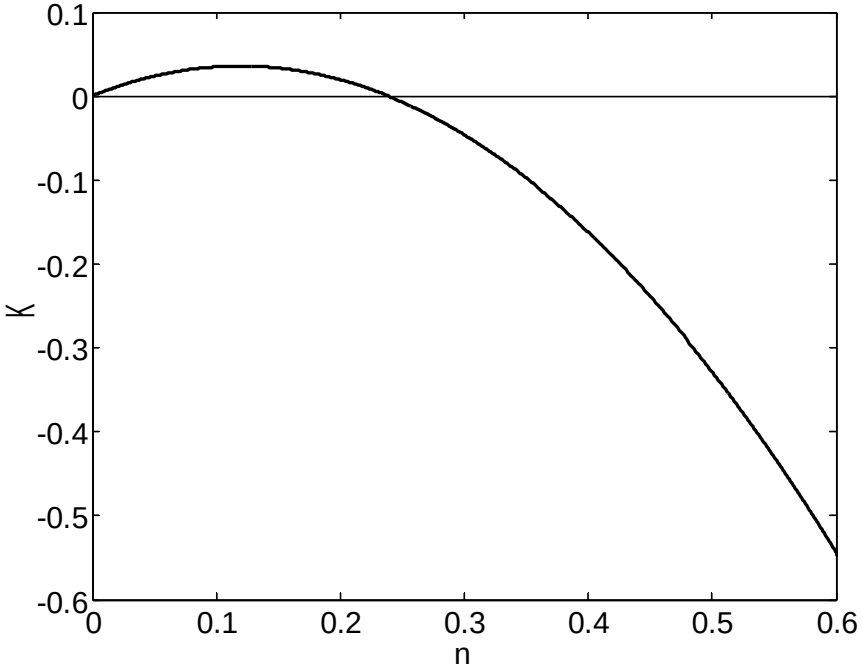
$$K = -V\frac{\partial P}{\partial V}$$

$$K = 8\left(-\frac{3}{4}n^{*2} + \frac{1}{3}\frac{n^*T^*}{(1-\frac{1}{3}n^*)^2}\right)$$

$$K = nkT - \frac{16}{3}\pi n^2\varepsilon\sigma^3\left(\frac{2}{3} + \frac{16\varepsilon}{105kT}\right)$$

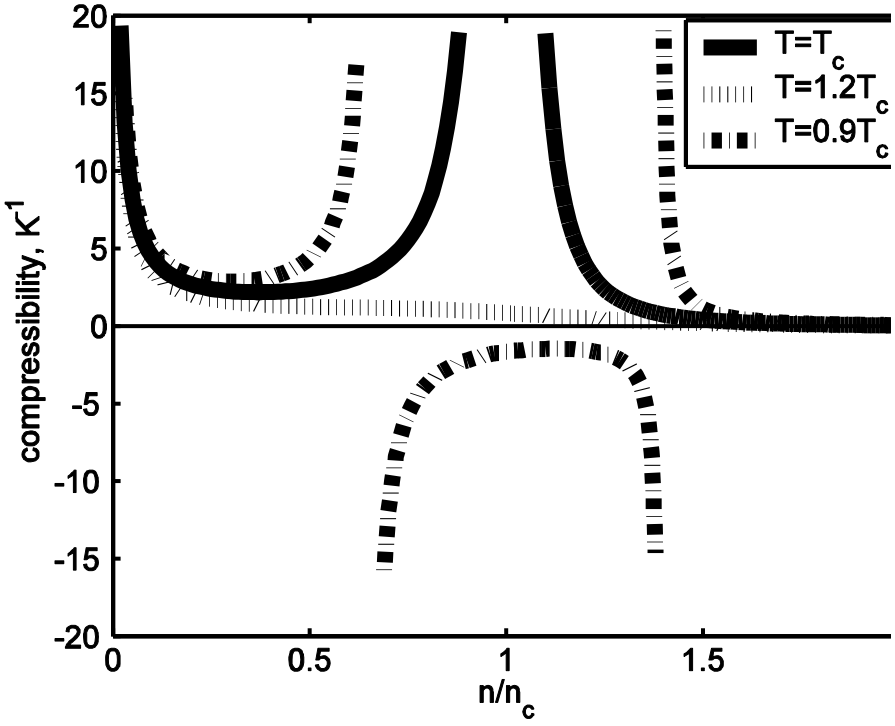


(b) inverse compressibility K



compressibility

Van der waals



artificial RDF